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High Pressure Stability, Transformation and Vibrational Dynamics of Nitrosonium Nitrate by Infrared and Raman Spectroscopy

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Beamline(s): U2A

Introduction: Nitrosonium nitrate (NO^+NO_3^-) was synthesized by laser heating of N_2O under high pressures in a diamond anvil cell. Synchrotron infrared absorption spectra of NO^+NO_3^- were measured at pressures up to 32 GPa at room temperature. Raman spectra were obtained at pressures up to 40 GPa at room temperature and up to 14 GPa at temperatures down to 80 K. For both lattice and intramolecular vibrational modes, a smooth evolution of spectral bands with pressure indicates that NO^+NO_3^- forms a single phase over a broad range above 10 GPa, whereas marked changes, particularly evident in the Raman spectra at low temperature, indicate a phase transition occurs near 5 GPa. At temperatures below 180 K, the NO^+NO_3^- species as found to persist at atmospheric pressure. The Raman and IR spectroscopic data suggest that the NO^+NO_3^- produced by laser heating of N_2O followed by decompression may differ in structure or orientational order-disorder from that produced by autoionization of N_2O_4 .

Methods and Materials: Pure N_2O gas was loaded cryogenically into a diamond anvil cell. The sample was pressurized to about 15 GPa and then heated by the 10.6 μm emission from a CO_2 infrared laser operated at about 50 W. The transformation of N_2O to NO^+NO_3^- was instantaneous at high temperature and irreversible when the sample was quenched to room temperature at high pressures. Infrared absorption measurements were performed at beamline U2A at the NSLS at BNL. Raman spectroscopy was performed at the Geophysical Laboratory.

Results: Figure 1 shows far infrared absorption spectra of NO^+NO_3^- collected at room temperature and seven selected pressures. The major feature in the far-IR is a broad band, peaking at 372 cm^{-1} at 32.5 GPa, with several shoulders at lower frequencies. This peak and the shoulders can be assigned to lattice modes of NO^+NO_3^- . The absorption intensity of the major lattice mode decreases with decreasing pressure. This trend resembles the IR activity previously seen in the mid-IR region, indicating that the ionic character of NO^+NO_3^- increases with compression. However, the far-IR lattice mode had not been observed previously, either in IR spectra of N_2O_4 at atmospheric pressure or of NO^+NO_3^- at high pressure.

Figure 2 shows the mid-IR spectra of NO^+NO_3^- obtained at room temperature and pressures ranging from 32.5 to 0.6 GPa. The region 1900-2200 cm^{-1} is omitted because of interference by strong absorption from the type II diamonds used by the pressure cell. At the highest pressure, 32.5 GPa, twelve IR bands are clearly resolved. Like the peak at 372 cm^{-1} observed in the far-IR region, that centered at 659 cm^{-1} is attributed to a lattice mode. The peaks observed at 761, 836 and 1133 cm^{-1} are assigned to vibrational modes of the NO_3^- anion, respectively ν_4 (E' , in plane bend), ν_2 (A_2'' , out of plane bend) and ν_1 (A_1' , symmetric stretch). The intense and broad peak centered near 1400 cm^{-1} is the most prominent feature in our IR spectra above 3 GPa, which was assigned to ν_3 , the NO_3^- asymmetric stretching mode.

Conclusions: We report the far- and mid- IR measurements of the ionic isomer NO^+NO_3^- at room temperature in high pressures up to 32 GPa in the spectral region from 100 cm^{-1} to 2500 cm^{-1} . Major IR-active modes are identified in the lattice and intramolecular regions as well as their combinations. The pressure dependence of all IR active modes was examined at room temperature. It is found that in the high-pressure region, NO^+NO_3^- is a crystalline phase. Our room temperature and low temperature Raman measurements both agree with previous studies of the transformation of N_2O_4 to NO^+NO_3^- . The low temperature measurements provide positive evidence of a phase transition for NO^+NO_3^- near 5 GPa.

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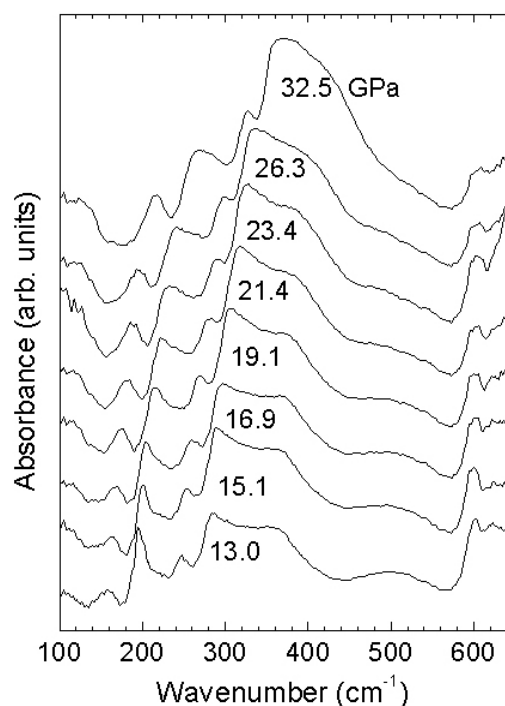


Fig 1. Far-IR spectra of NO^+NO_3^- in the range $100\text{--}600\text{ cm}^{-1}$ measured at room temperature for seven pressures labeled in GPa. At each pressure, the absorbance has been normalized to the beam current of the synchrotron light source.

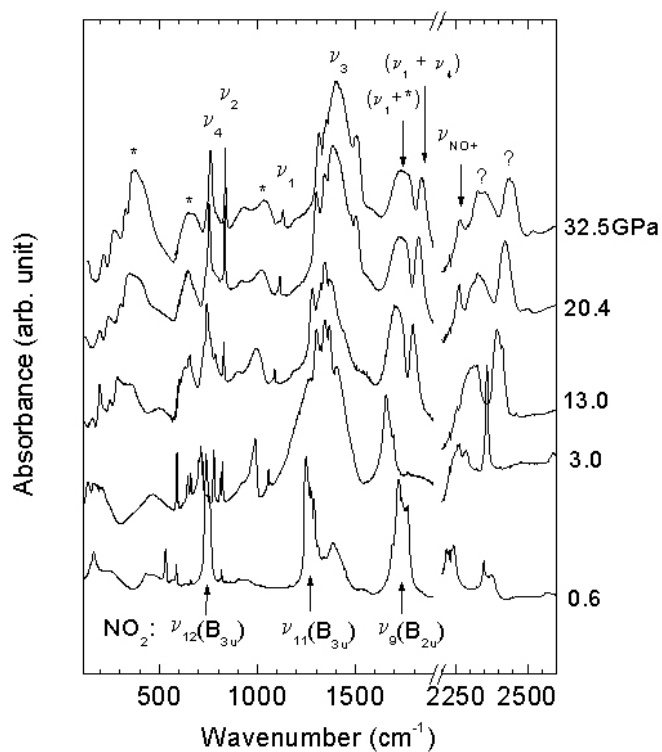


Fig 2. IR spectra of NO^+NO_3^- in the range $100\text{--}2500\text{ cm}^{-1}$ measured at room temperature for five pressures (indicated in GPa on right hand ordinate). The absorbance has been normalized with respect to the beam current of the synchrotron light source. The sample thickness was about $23\text{ }\mu\text{m}$. The region $1900\text{--}2200\text{ cm}^{-1}$ is omitted because of interfering absorptions from the Type II diamonds are used in the anvil cell. Asterisks (*) indicate lattice modes or combinations.